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Extraction of Free Fatty Acid Mixtures from Rice Bran Oil by Aqueous Renewable Alcohols: Liquid-liquid Equilibrium Diagram and Number of Equilibrium Stages

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Highlights:

- Mixed fatty acids have lower distribution coefficients
- The required number of extraction stages is in the 1-8 range
- Aqueous isopropanol is a better solvent than aqueous ethanol

Abstract. This work is aimed to measure the liquid-liquid equilibria of rice bran oil-fatty acid-aqueous alcohols using fatty acid mixtures derived from rice bran oil as solutes and to calculate the number of equilibrium stages required for the extraction process. Renewable alcohols, ethanol and isopropanol in aqueous form were used as solvents. The liquid-liquid equilibrium data were measured at 25 °C and presented as ternary diagrams. It was found that ethanol gave a lower distribution coefficient than isopropanol. For the same solvent, increasing the water content resulted in a lower distribution coefficient. For the free fatty acid contents of 30% in the feed and of 10% to 2.5% in the raffinate, the minimum solvent-to-feed ratio was found to be in the range of 1 to 5. Using solvent-to-feed ratios from 2 to 4, the number of extraction stages required was in the range of 1 to 8. Based on the minimum solvent-to-feed ratio and number of equilibrium stages, isopropanol was found to be better than ethanol.

Keywords: *equilibrium stage; fatty acid mixture; renewable alcohol; rice bran oil; solvent extraction.*

1 Introduction

Conventional rice mills separate rice seeds into three fractions, i.e. white rice husk, and bran. These fractions contribute about 70%, 20%, and 10% of rice weight respectively. As written by Luh in [1] and Shahidi in [2], rice bran consists of 15~18% oil, 0.4~1.5% wax, 5~8% protein, 40~50% soluble carbohydrate, and 5~8% fiber. Rice bran oil (RBO) is healthy vegetable oil, containing vitamins, antioxidants, nutrients, and trans-fat free oil, as reported by Cheong and Xu in

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[3]. RBO is vastly superior to traditional cooking oils and can be considered a nutraceutical oil. It contains unique components, such as oryzanol and tocotrienol, which have drawn people's attention. Numerous studies show that RBO reduces harmful cholesterol without reducing good cholesterol. Oryzanol is the key element responsible for that function, as reported by Sugano and Tsuji in [4], Sugano*, et al.* in [5], Schaffer*, et al.* in [6], and Theriault*, et al.* in [7]. Tocotrienol, on the other hand, is highlighted by Schaffer, *et al.* in [6] as the most precious vitamin E existing in nature and is said to have an anti-cancer effect too. It has been suggested to suppress the production of reactive oxygen species more efficiently than tocopherols. RBO is rich not only in α-tocopherol but also has the highest amount of tocotrienol in liquid form. As reviewed by Garba, *et al.* in [8], applications of RBO can be found in foods, pharmaceuticals and cosmetics. Further interests in utilizing rice bran oil can be seen from the many recent efforts in finding new uses of rice bran oil, in the health sector as reported by Devarajan, *et al.* in [9], in the food sector as reported by Gupta *et al.* in [10], in the packaging sector as reported by Kale, *et al.* in [11], in the chemical sector as reported by Salinas-Solano, *et al.* in [12], and in the bioenergy sector as reported by Ihoeghian and Usman in [13], Nguyen, *et al.* in [14], and El Khatib, *et al.* in [15].

As commonly applied to other vegetable oils, the purification of crude RBO includes dewaxing and degumming, deacidification or free fatty acid (FFA) removal, bleaching, and deodorization. The drawback of crude RBO is the fact that it contains a lot of FFAs due to enzymatic activity in the rice bran itself. The conventional deacidification methods to remove FFAs from vegetable oils include distillation, neutralization, and miscella, which have been reviewed by Cheong and Xu in [3], Ghosh in [16], Bhosle and Subramanian in [17]. Neutralization using caustic soda removes FFAs as soap. This method, however, results in a high loss of neutral oil and nutrients, especially antioxidants. Distillation carried out at a high temperature is energy-intensive and has other disadvantages, including the alteration of color and essential nutraceuticals. Miscella deacidification is a chemical method that is applied to the extract. It has to be done in a very tightly closed system since the extract is as volatile as the solvent. Alternatives for removing FFA from vegetable oils that are still under development include catalytic esterification as reported by Habaki, *et al.* in [18], enzymatic esterification as reported by Wang*, et al.* in [19], enzymatic amidation as reported by Wang, *et al.* in [20], membrane separation as reported by Azmi, *et al.* in [21] and Firman, *et al.* in [22], deep eutectic ionic liquid extraction as reported by Zullaikah, *et al.* in [23] and Zahrina, *et al.* in [24], and liquid-liquid extraction using volatile organic solvents, which is known as solvent extraction.

For removing FFAs from vegetable oils, solvent extraction is known to be a potential alternative to the conventional methods, as revealed by Albuquerque, *et al.* in [25]. The solvents that are mentioned to be suitable for this application are

short-chain alcohols, among others ethanol and isopropanol. In aqueous form, these two alcohols are immiscible with vegetable oil but solubilize free fatty acids. They are also renewable, opening opportunities for a more sustainable process. As fundamental data for designing solvent extraction processes, liquid-liquid equilibria (LLE) of the vegetable oil-FFA-solvent systems, including rice bran oil, have been published. Apelblat, *et al.* [26] studied soybean and jojoba oils using various solvents, including N-methylformamide, formamide, dimethylsulfoxide, 1,2-butanediol, and 2-butene-1,4-diol. Batista, *et al.* in [27] and in [28], Mohsen-Nia and Dargahi in [29], Silviana in [30], and Mohsen-Nia and Khodayari in [31] and Busto and Vera in [32] studied canola, corn, palm, and sunflower oils, respectively, using anhydrous alcohols as solvents. Using aqueous ethanol as solvent, Gonçalves, *et al.* in [33], Gonçalves and Meirelles in [34], da Silva, *et al.* in [35], Chiyoda, *et al.* in [36], Cuevas, *et al.* in [37], and Rodrigues and Meirelles in [38] have reported LLE on corn oil, palm oil, palm oil fractions, soybean oil, sunflower oil, and peanut and avocado seed oils, respectively. Rodrigues, *et al.* [39-41] studied RBO using aqueous ethanol as solvent including the effects of antioxidants. All of these previous works were carried out using single fatty acids (palmitic acid, stearic or oleic acid), commercial oleic acids or commercial linoleic acids as solutes.

In real applications, deacidification is applied to vegetable oils containing fatty acid mixtures formed by the enzymatic hydrolysis of the oils. The major fatty acids in vegetable oil, rice bran oil, for example, are palmitic (12%-18%), oleic (40%-50%), and linoleic (29%-42%) acids, as stated by Shahidi in [2]. The commercial oleic acids used by Batista *et al.* in [27] and in [28], Mohsen-Nia and Dargahi in [29], Mohsen-Nia and Khodayari in [31], Gonçalves, *et al.* in [33], da Silva, *et al.* in [35], Rodrigues and Meirelles in [38], Rodrigues, *et al.* in [39], Rodrigues, *et al.* in [40], and in [41] were already multicomponent but still dominated by oleic acid (77% to 80%). So was the commercial linoleic acid used by Chiyoda, *et al.* in [36], which was dominated by linoleic acid. Shah and Venkatesan in [42] used mixed fatty acids from groundnut oil. However, their work mainly presented phase separation data. Oliveira, *et al.* in [43] measured and correlated the LLE of degummed RBO (containing 5%-wt FFA)-aqueous ethanol and applied their correlation to predict the extraction of oil from rice bran using ethanol *(solid-liquid extraction)*. However, they measured the data without variation of FFA contents in the RBO so that complete LLE diagrams could not be constructed although the solvent-to-RBO ratios had been varied during the measurement. Lima, *et al.* [44] studied LLE of olive oil-FFA-ethanol-water using FFA derived from olive oil. However, most of their data involved only three of the four components studied and, in the quaternary system, the concentrations of FFA and olive oil were lumped into one group. The concentration of solute needs to be separated to allow extraction performance evaluation. Furthermore, the number of liquid-liquid extraction stages required was not mentioned. Complete

composition data using fatty acid mixtures derived from the corresponding vegetable oils are necessary for more accurate calculations. The number of equilibrium stages is also necessary for determining the dimension of the extractors. It is the purpose of this work to measure the LLE data and construct the LLE diagram of vegetable oil-mixed FFAs-aqueous alcohol systems and to calculate the number of equilibrium extraction stages for removing FFAs from vegetable oils. The works were specifically aimed to study RBO-mixed FFAs-aqueous ethanol and RBO-mixed FFAs-aqueous isopropanol systems. RBO was considered since it has very high potential to be produced in Indonesia as Indonesia is the third-largest producer of rice in the world with an annual production of more than 83 million tons of rice crops (paddy) in 2018, as reported by FAO in [45].

2 Experiment

2.1 Materials

Ethanol (CAS number 64-17-5, anhydrous, ≥99.5%) and isopropanol (CAS number 67-63-0, anhydrous, ≥99.5%), were purchased from Sigma Aldrich. Potassium hydroxide (CAS number 1310-58-3, for analysis, ≥85%) was purchased from Merck. RBO (CAS number 68553-81-1) and sulfuric acid (CAS number 7664-93-9, industrial grade, 98%) were purchased from a local supplier.

2.2 Saponification

FFA was obtained by saponifying RBO. RBO of 500 g was mixed with 750 mL potassium hydroxide solution in aqueous ethanol (95% volume ethanol). The quantity of potassium hydroxide was determined from the saponification value of RBO that was found to be 188 mg KOH/g and with an excess of 10%. The mixture was refluxed in four hours, cooled, and acidulated using sulfuric acid. The mixture was then transferred into a separation funnel. The upper oil phase was washed three times using warm water and then distilled under vacuum to remove any residual water to obtain FFA which is hereafter called RBO FFA.

2.3 Apparatus and Procedure

The measured LLE data included binodal curves and tie-lines. Binodal curves were measured by titration and turbidity observation, according to Ardila, *et al.* [46]. Figure 1 presents a schematic of the experimental apparatus used. It consisted of a jacketed equilibrium cell (made of glass having a volume of 50 cm^3), a 10 cm^3 burette with a scale reading of 0.02 cm^3, and an insulated water batch. The equilibrium cell was placed on a magnetic stirrer to allow complete homogenization of the observed mixture. The temperature inside the equilibrium

cell was read using a digital thermometer TENMARS TM-747DU with an uncertainty of 0.1°C. The temperature of the circulated water was controlled at 25 °C using an Ellitech STC-1000 temperature controller connected to an immersion heater and a handy cooler. The water bath was equipped with an agitator to homogenize the water temperature.

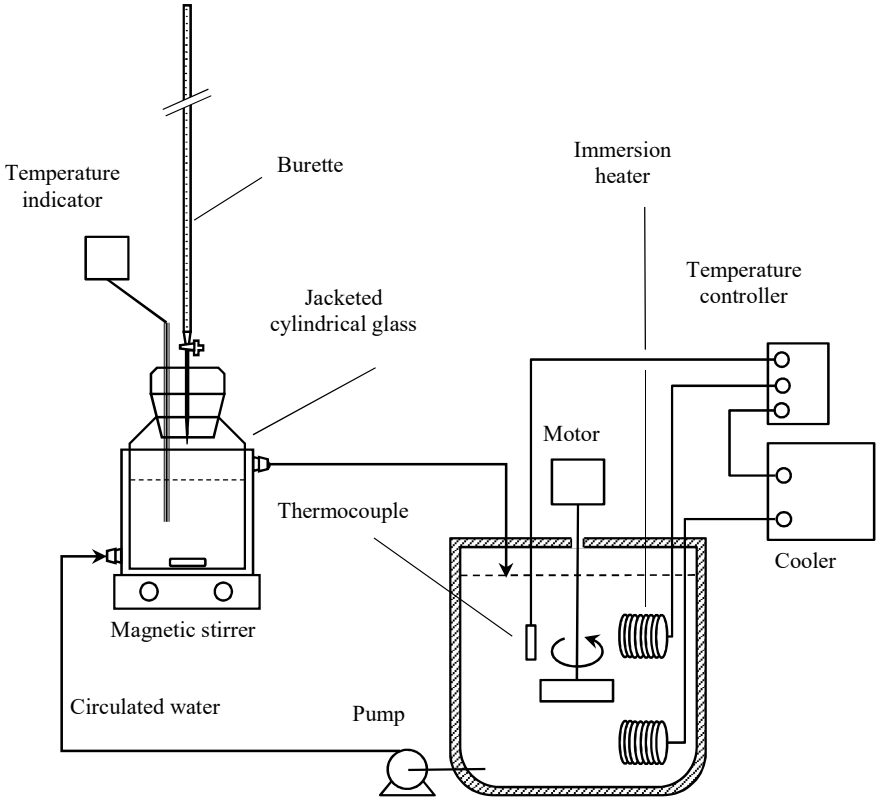

Figure 1 Schematic diagram of the experimental apparatus.

Detail flowcharts of measurement procedures can be found in Figures S1 and S2 in Supporting Information. The binodal curve on the oil side was observed by titrating a homogeneous mixture of RBO and FFA with solvent. The binodal curve on the solvent side was followed by titrating a homogeneous mixture of solvent and FFA with RBO. The titration was stopped when the mixture started becoming turbid. The composition was then calculated from the material balance. Tie-lines were measured by the same cell that was used to measure the binodal curves but without installing a burette. An RBO-FFA mixture, prepared by

blending RBO and RBO FFA, at a determined blending ratio, was mixed with a solvent in the cell at an equal weight ratio and then stirred vigorously. The mixture was aged in a day to achieve an equilibrium condition and then separated to obtain extract and raffinate phases. Solvent (alcohol and water) was removed from each phase by vacuum vaporization to get solvent-free extract and raffinate. The weight of solvent in the extract (raffinate) could be obtained by weighting the extract (raffinate) twice, before and after vacuum evaporation. The FFA contents of the solvent-free extract and raffinate were measured as acid values. The binodal curves and tie-lines were represented in weight fraction. To do this, the molecular weight of FFA was necessary. In this research, the molecular weight of FFA was calculated from the composition of RBO FFA. The validity of the measurement was checked using oleic acid as solute and ethanol as solvent. A good agreement between the experimental data and literature was found, as shown in Figure S3 in Supporting Information. The uncertainty in weight fraction was estimated to be 0.0032 from replicated runs.

2.4 Analysis

Acid value, saponification value, titer, and iodine value were measured according to the IUPAC standards as described by Paquot in [47]. Fatty acids in the form of methyl ester were analyzed using a Shimadzu 2010-GCMS-QP2010 Ultra with an RtX®-5MS capillary column (30 m length, 0.25 mm ID, and 0.25 μm film thickness).

3 Results and Discussion

3.1 Characteristic of Free Fatty Acid

The FFA derived from RBO was found to have an acid value of 196 mg KOH/g, an iodine value of 91 g I_2/100 g, and a titer of 29 °C. The high acid value ensured that the RBO was saponified completely. The primary fatty acids found were palmitic (21.3%), stearic (3.2%), oleic (42.5%), and linoleic (28.8%) acids. As expected, this composition was different from that of commercial oleic acids. A commercial oleic acid, as used by Rodrigues, *et al.* in [39], contained 5.4% palmitic acid, 1.4% stearic acid, 78.0% oleic acid, and 12.0% linoleic acid. The RBO FFA, as derived here, clearly included more saturated fatty acids (palmitic and stearic acids) than commercial oleic acid.

3.2 Equilibrium Data

The LLE data of RBO-RBO FFA-solvent are illustrated as ternary diagrams shown in Figures 3 to 6. The distribution coefficients of FFA using ETH80 (80%-w ethanol), ETH90 (90%-w ethanol), IPA80 (80%-w isopropanol), and IPA90

(90%-w isopropanol) as solvents were found in the *0.15~0.65*, *0.61~0.91*, *0.45~0.84*, and *0.97~0.99* ranges, respectively. The distribution coefficient is defined as the ratio of weight fraction of FFA in the extract to that in the raffinate.

As discussed by Ginting, *et al.* [48], it is necessary to check the consistency of the measured tie-line data using the Bachman-Brown correlation. Bachman in [49] and Brown in [50] proposed equations for correlating weight fractions of nonconsolute components in the systems with a single pair of nonconsolute components and two pairs of nonconsolute components, respectively. As the systems studied here formed a single pair of nonconsolute components, the Bachman correlation was adopted. Here, the Bachman correlation is expressed as

$$x_{RBO,R} = A\,(x_{RBO,R}/x_{S,E})\; + B \tag{1}$$

where $x_{RBO,R}$ is the weight fraction of RBO in the raffinate (RBO rich phase), $x_{S,E}$ is the weight fraction of solvent in the extract (solvent rich phase), and A and B are correlation constants. Consistent data exhibit a linear relation as given by Eq. (1). Figure 2 presents the Bachman-Brown correlation for the RBO-RBO FFA-aqueous alcohol systems. The experimental tie-line data for all solvents could be fit well by Eq. (1) with correlation coefficients in the range of 0.999 to 1.000. This confirmed that the experimental data were consistent.

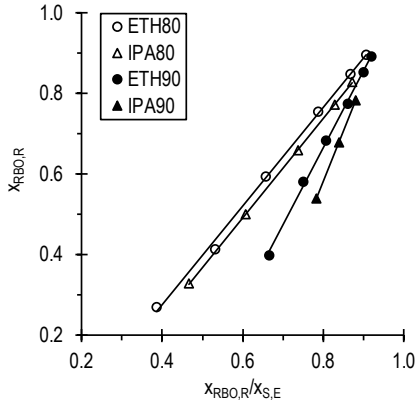

Figure 2 Bachman-Brown correlation for RBO-FFA-aqueous alcohol systems.

It is interesting to compare the ternary diagram developed using an RBO FFA to that using an FFA model from the literature. The comparison is shown in Figure 3 for 90%-w ethanol as a solvent. The data were taken from Rodrigues, *et al.* in [39] who used commercial oleic acid as FFA. It can be seen that the binodal curve on the raffinate side was a little bit different. Besides, the tie-lines using commercial oleic acid as an FFA model were flatter than that using RBO FFA

(Figure 3). These results in a slightly higher distribution coefficient for the case of oleic acid as a fatty acid model. Using 90%-w ethanol as solvent at 25 °C, the distribution coefficient of commercial oleic acid is in the 0.78~0.92 range, estimated from the data of Rodrigues, *et al.* in [39]. Besides oleic acid, RBO FFA also contains palmitic and stearic acids, 24.5%, as found here. These two fatty acids have lower solubility than oleic acid, causing the distribution coefficients of RBO FFA to be lower than those of commercial oleic acid. The relative differences of distribution coefficients were found in the 2%-20% range; the closer the tie-line to the *plait point* the larger the difference. For preliminary designs, especially when the conditions are far from the *plait point*, these differences are acceptable, meaning that oleic acid is relatively representative for FFA in RBO. For detailing the designs, however, it is better to use FFAs data derived from the corresponding vegetable oils.

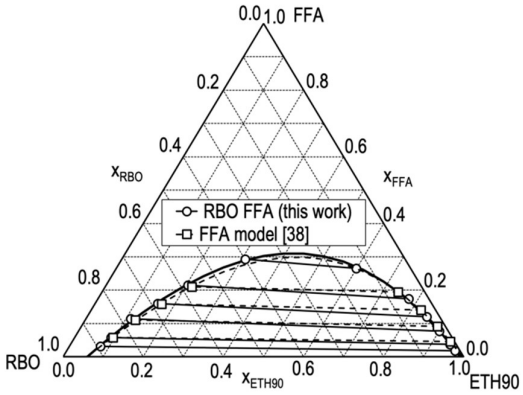

Figure 3 LLE of RBO-RBO FFA-ethanol 90%-w (ETH90).

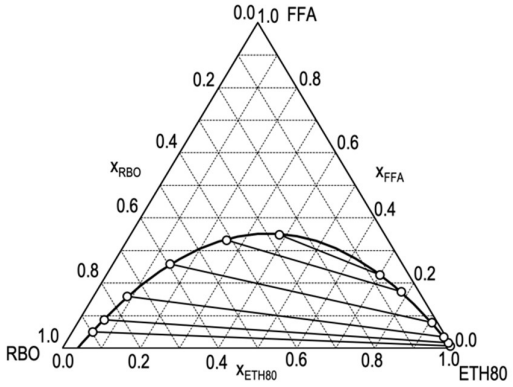

Figure 4 LLE of RBO-RBO FFA-ethanol 80%-w (ETH80).

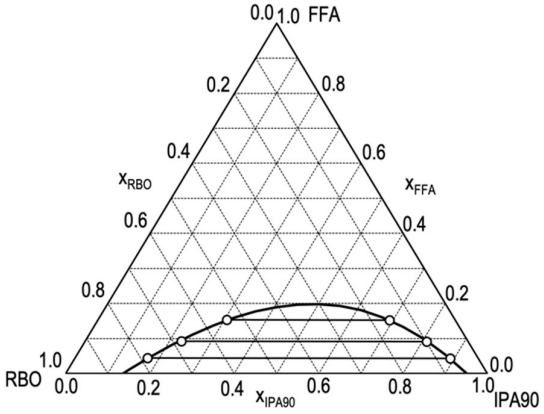

Figure 5 LLE of RBO-RBO FFA-isopropanol 90%-w (IPA90).

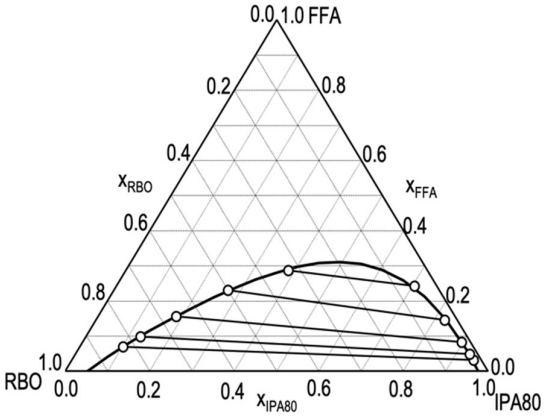

Figure 6 LLE of RBO-RBO FFA-isopropanol 80%-w (IPA80).

Higher water content resulted in a wider two-phase area (Figure 3 vs. Figure 4 and Figure 5 vs. Figure 6). The distribution coefficients of RBO FFA under the conditions studied here were lower than one, as also indicated by the tie-lines which became lower toward the extract side. Increasing the water content in the solvents lowered the distribution coefficient significantly. The same was also observed using commercial oleic acids by Batista, *et al.* in [27], Gonçalves, *et al.* in [33], da Silva, *et al.* in [35], Rodrigues, *et al.* in [39]. A higher water content in the solvent depresses miscibility and hence extends the two-phase region. In addition, lower miscibility decreases solubility and therefore decreases the distribution coefficient. For the same water content, isopropanol has a narrower two-phase area but exhibits higher distribution coefficients, 0.15~0.65 vs. 0.45~0.84 at 20%-w water and 0.61~0.91 vs. 0.97~0.99 at 10%-w water.

Isopropanol and ethanol have normalized solvent polarities of 0.546 and 0.654, respectively, as known from Reichardt in [51]. The less polar solvent dissolves more oil, including FFAs, and gives a greater distribution coefficient.

3.3 Number of Extraction Stages

By using the ternary diagrams developed, a series of equilibrium calculations for extracting FFA from RBO was carried. The calculations were carried out using a graphical method, according to Coulson and Harker in [52]. Figure 7 presents a typical graphical estimate where R and E stand for raffinate and extract, respectively, and blue and red lines represent equilibrium and operating lines, respectively. The FFA in the feed ($x_{FFA,F}$) was assumed to be 30% and that in the product or deacidified RBO ($x_{FFA,P}$) was varied from 2.5% to 10% (solvent-free bases).

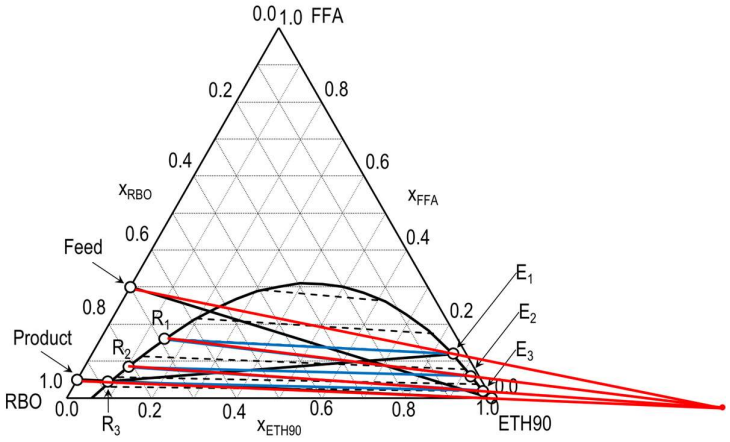

Figure 7 Graphical calculation of equilibrium stage (ethanol 90%-w, S/F = 2).

Table 1 presents the minimum solvent-to-feed (S/F) ratio at various solvent and FFA content in the products. It is clearly shown that a higher water content resulted in a higher minimum S/F ratio. IPA exhibited a lower minimum solvent-to-feed ratio than ethanol. These two results were closely related to the distribution coefficient. A lower distribution coefficient results in a higher minimum S/F ratio. In addition, the lower the FFA content in the product, the higher the minimum S/F ratio since the separation task becomes more difficult at a lower FFA content in the product.

Table 2 shows the estimated number of equilibrium extraction stages with solvent ratios of 2 to 5. Stage calculations at an S/F ratio of 2 could not be done for ETH80 at all FFA contents in the products. Moreover, stage calculations at an S/F of 4

could be done only at 10% FFA content in the product. Considering the increasing number of equilibrium stages, the solvent can be ordered as IPA90, ETH90, IPA80, and ETH80. The lower the FFA content in the product, the more extraction stages required. About 1 to 8 extraction stages were needed for ETH90, IPA80, and IPA90 to lower the FFA in RBO from 30% to 2.5%. The higher the S/F ratio, the lower the number of stages. At the same water content, solvent-to-feed ratio, and content of FFA in the product, isopropanol gave a lower minimum solvent ratio and a smaller number of equilibrium stages. Isopropanol is therefore better than ethanol for extracting FFA from RBO. In addition, isopropanol has a higher boiling point than ethanol, i.e. 83 ºC and 78 ºC, respectively, signifying that isopropanol is also less flammable and safer than ethanol. Of course, a deeper study, which includes economic feasibility, needs to be undertaken to convince which solvent is better.

Table 1 Minimum solvent ratio.

$x_{FFA,P}$	ETH80	ETH90	IPA80	IPA90
10.0%	2.5	1.0	1.4	1.0
5.0%	4.1	1.2	1.6	1.0
2.5%	4.7	1.4	1.8	1.0

Table 2 Number of equilibrium stages.

Solvent:	ETH80		ETH90		IPA80		IPA90	
S/F:	4	5	2	4	2	4	2	4
$x_{FFA,P} = 0.100$	3	2	2	1	3	2	2	1
$x_{FFA,P} = 0.050$	-	4	3	2	5	3	2	2
$x_{FFA,P} = 0.025$	-	6	4	3	8	3	3	2

4 Conclusions

Liquid-liquid equilibria of rice bran oils-fatty acids-aqueous alcohols using fatty acid mixtures derived from rice bran oils were measured. Isopropanol was found to give higher distribution ratios but a narrower two-phase region in comparison to ethanol. Compared to the systems using commercial oleic acid to represent fatty acid mixtures, lower distribution coefficients were found using mixed fatty acids from rice bran oils. For free fatty acid contents of 30% in the feed and of 2.5% to 10% in the deacidified rice bran oil, the minimum solvent-to-feed ratio was found to be in the range of 1 to 5. In addition, using solvent-to-feed ratios between 2 to 4, the number of equilibrium extraction stages required was in the range of 1 to 8. Based on the minimum solvent-to-feed ratio and number of equilibrium stages, isopropanol was found to be better than ethanol.

Nomenclature

A	=	constant Eq. (1)
B	=	constant Eq. (1)
$x_{FFA,F}$	=	weight fraction of FFA in feed
$x_{FFA,P}$	=	weight fraction of FFA in product
$x_{RBO,R}$	=	weight fraction of RBO in raffinate
$x_{S,E}$	=	weight fraction of solvent in extract
S/F	=	solvent-to-feed ratio

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